PATENT SPECIFICATION (11) 1435744

1435744

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(61) Patent of Addition to No. 1402751 dated 25 Feb. 1972
(31) Convention Application No. 2230743 (32) Filed 23 June 1972 in
(33) Germany (DT)
(44) Complete Specification published 12 May 1976
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(19) THE PATENT OFFICE LONDON

(54) AMPHOLYTE MIXTURES

START ON NEXT PAGE

(71) I, NIKOLAUS GRUBHOFER, of German Nationality, of Gustav-Kirchhoff-Strasse 12, D-69, Heidelberg, Germany, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in and relating to ampholytic materials and, more particularly is concerned with an improvement in or modification of the invention described in Specification No. 1,402,751.

In Specification No. 1,402,751 there is described ampholytic material comprising a mixture of ampholytes which are polyamines containing at least four primary, secondary or tertiary amino groups, as basic groups, and at least one sulphonic acid or sulphoester group, as acid group. Some of the amino groups may be quaternised and after the application of an electric field and stabilization of the aqueous phase by means of a carrier or membranes it has been found that the mixtures, have a pH gradient between pH 2 and pH 12. Specification No. 1,402,751 also describes methods for manufacturing such ampholytic materials.

It has now been found, in accordance with the present invention that the acid group of the ampholytes may be wholly or partially replaced by phosphonic acid groups. Thus, the ampholytes may contain as acidic groups, phosphonic acid groups or sulphonic and phosphonic acid groups and, additionally, may also contain carboxylic acid groups.

The ampholyte mixtures according to the present invention in which ratio of basic to as compared with more conventional ampholytic materials.

1) The acidic groups used give the resultant aminosulphonic acids and amino-phosphonic acids as other buffer zones and thus cover the zones which are only imperfectly covered by the aminocarboxylic acids.

2) The acids are generally more disassociated than the carboxylic acids and thus allow for a lower pH range than the aminocarboxylic acids.

3) The amino-phosphonic acids, more particularly in combination with amino-sulphonic acids, have substantially lower bonding capacities in respect of heavy metals than the aminocarboxylic acids. (N. E. Good *et al* (1966), Biochemistry 5,467—477).

The ampholyte materials of the invention may be prepared by reacting an aqueous polyamine solution, preferably an aliphatic polyamine solution, with an aqueous solution of a phosphonic acid or phosphonate salt and, if desired, a sulphonic acid or salt thereof, if desired in the presence of an antioxidant or catalyst. The polyamine may first be alkylated, e.g. by reaction in aqueous solution with a neutral alkylating agent such as dimethyl sulphate or by reacting in alcohol solution with an alkyl halide, the reaction products being recovered from the resultant acid reaction by-product by treatment with a cation exchange resin.

The introduction of phosphonic acid groups into the polyamines may be effected by reacting them with chloromethylene phosphonic acid in a manner analogous to that described in US Patent 2,841,611. The following scheme illustrates a typical reaction between 1

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SPECIFICATION NO 1435744

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(54) AMPHOLYTE MIXTURES

(71) I, NIKOLAUS GRUBHOFER, of German Nationality, of Gustav-Kirchhoff-Strasse 12, D-69, Heidelberg, Germany, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improvements in and relating to ampholytic materials and, more particularly is concerned with an improvement in or modification of the invention described in Specification No. 1,402,751.

In Specification No. 1,402,751 there is described ampholytic material comprising a mixture of ampholytes which are polyamines containing at least four primary, secondary or tertiary amino groups, as basic groups, and at least one sulphonic acid or sulphoester group, as acid group. Some of the amino groups may be quaternised and after the application of an electric field and stabilization of the aqueous phase by means of a carrier or membranes it has been found that the mixtures, have a pH gradient between pH 2 and pH 12. Specification No. 1,402,751 also describes methods for manufacturing such ampholytic materials.

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It has now been found, in accordance with the present invention that the acid group of the ampholytes may be wholly or partially replaced by phosphonic acid groups. Thus, the ampholytes may contain as acidic groups, phosphonic acid groups or sulphonic and phosphonic acid groups and, additionally, may also contain carboxylic acid groups.

The ampholyte mixtures according to the present invention in which ratio of basic to acidic groups is different in different ampholytes possess the following advantages as compared with more conventional ampholytic materials.

1) The acidic groups used give the resultant aminosulphonic acids and amino-phosphonic acids as other buffer zones and thus cover the zones which are only imperfectly covered by the aminocarboxylic acids.

2) The acids are generally more disassociated than the carboxylic acids and thus allow for a lower pH range than the aminocarboxylic acids.

3) The amino-phosphonic acids, more particularly in combination with amino-sulphonic acids, have substantially lower bonding capacities in respect of heavy metals than the aminocarboxylic acids. (N. E. Good *et al* (1966), Biochemistry 5,467—477).

The ampholyte materials of the invention may be prepared by reacting an aqueous polyamine solution, preferably an aliphatic polyamine solution, with an aqueous solution of a phosphonic acid or phosphonate salt and, if desired, a sulphonic acid or salt thereof, if desired in the presence of an antioxidant or catalyst. The polyamine may first be alkylated, e.g. by reaction in aqueous solution with a neutral alkylating agent such as dimethyl sulphate or by reacting in alcohol solution with an alkyl halide, the reaction products being recovered from the resultant acid reaction by-product by treatment with a cation exchange resin.

The introduction of phosphonic acid groups into the polyamines may be effected by reacting them with chloromethylene phosphonic acid in a manner analogous to that described in US Patent 2,841,611. The following scheme illustrates a typical reaction between 1 mole of pentaethylene hexamine and 4 moles of chloromethylene phosphonic acid.

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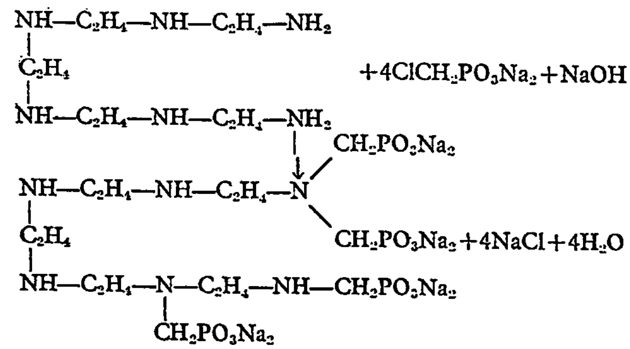

The alkaline medium used in this case was sodium hydroxide solution since precipitations occur if barium hydroxide is used as alkaline medium. The sodium ion may be removed after the reaction is completed with the aid of a highly cross-linked —20% DVP styrene-divinylbenzene sulphonic acid exchanger. The use of this exchanger ensures that in practice, there is no absorption of finished ampholytes.

In order that the invention may be well understood reference will be made to the accompanying drawings which are graphical representations of buffer capacity against pH for various ampholytic materials in accordance with the invention.

Figure 1 shows the relationship of buffer capacity to pH in the case of an amino-phosphonic acid ampholyte manufactured by reacting 0.5 mole phosphonic acid per atom of nitrogen, and clearly shows that the buffer capacity is particularly good over the whole pH range. Buffer capacity (Bc) is defined as the millival quantity (i.e. the amount in milliequivalents) of acid or lye which causes a pH displacement of 1 unit for 1 milligramme-mole ampholyte mixture. Ampholyte-molarity is calculated from nitrogen content as estimated by the Kjeldahl method.

In practice the ampholytic materials will generally contain both sulphonic acid and phosphonic acid and phosphonic acid groups and it is possible to introduce carboxyl groups.

In practice sulphonic acid/phosphonic acid ampholytes are manufactured by reacting the polyamine first with chloromethylene phosphonic acid, suitably in a mole ratio of 1 mole of nitrogen to 1/6 mole of chloromethylene phosphonic acid. With this amount of chloromethylene phosphonic acid the alkaline pH of the amine itself is sufficient to complete the reaction. The sulphonic acid groups are introduced with a sultone such as propane sultone which is used in conjunction with barium hydroxide (catalyst) which now causes no precipitation to occur. Phosphonic acid/sulphonic acid/carboxylic acid combinations may be easily manufactured by allowing the aminosulphonic-phosphonic acid ampholyte to react in known manner with an acid such as acrylic acid Figures 2 and 3 show characteristic pH buffer capacity distributions of an amino-phosphonic sulphonic acid and an amino-phosphonic-sulphonic-carboxylic acid respectively.

It is obvious that the availability of two further types of acidic groups and also the possible partial quarternisation of the amino groups makes it possible to produce a whole variety of novel ampholytic buffer materials, and it seems possible with these to more closely approach the ideal ampholyte mixture, namely a mixture which has a completely constant buffering capacity over at least the pH range between pH 3 and pH 10, irrespective of the pH. With regard to Figures 1 and 2, it will be seen that by carrying out the reaction in a suitable manner or by mixing several components, the ampholyte mixtures are obtained on the basis of aminophosphonic acid sulphonic acid and already meet this requirement to a very satisfactory extent.

In order that the invention may be well understood the following Examples are given by way of illustration only.

Example 1
Manufacture of aminophosphonic acid mixtures

560 grammes of pentaethylene hexamine are mixed with 3 litres of water and 500 ml of 50% sodium hydroxide solution and these are added to 1,300 grammes of disodium chloromethylene phosphonate in 3 litres of water. The reaction mixture is then refluxed for 15 hours. After cooling and filtering the mixture is diluted to 30 litres and percolated through a column (30 cm diameter) filled with 40 l Zeo-KARB SRC-21 (hydrogen form; the word "Zeo-KARB" is a Registered Trade Mark). The vitually colourless solution is then concentrated to approximately 15 l and then subjected to fractional electrodialysis.

Each 2,100 cc (100 cc/cell) are separated in the separating vessels at 100 to 150 V (not exceeding 60 mA) for 48 hours. The individual fractions are removed separately and identical volumes are concentrated from cells 3 to 17.

Example 2

Manufacture of aminophosphonic acid-sulphonic acid mixtures

560 grammes of pentaethylene hexamine are mixed with 3 litres of water and 300 grammes chloromethylene phosphonic acid to give pH 10 which is then refluxed for 15 hours. The mixture is then reacted with 3 litres of a solution of 750 grammes of barium hydroxide octahydrate and raised to a temperature of 60°C. 600 grammes of propane sultone in 400 cc of acetone are then added dropwise, the temperature being maintained at 60°C. After 4 hours the barium is precipitated out by the addition of approximately 2,400 cc of 2N-H_2SO_4, centrifuged and given a thorough washing in the centrifuge. It is necessary to concentrate the mixture to approximately half its volume, after which it is subjected to electrodialysis in known manner.

Example 3

Manufacture of aminosulphonic acid-carboxylic acid mixtures

3 litres of an approximately 20% aqueous solution of aminosulphonic/phosphonic acid ampholyte prepared according to Example 2 are heated to 50°C. 400 ml of a 50% aqueous solution of acrylic acid are added over a period of 1 hour and the solution is kept at 50°C for 15 hours. Without further purification and fractionation the material gives the buffer capacity/pH curve shown in Figure 3.

Example 4

Alkylation of a polyamine

230 grammes (1 mole) of pentaethylene hexamine are dissolved in 20 litres of methanol and refluxed with 250 grammes (2 mole) of dimethyl sulphate and boiled for 4 hours. 5 litres of water are added to the mixture which is then reduced to half its volume under reduced pressure. The solution is then percolated over 5 litres of a strongly basic ion exchanger (Dowex 1X8; the word "Dowex" is a Registered Trade Mark) in order to bond the resultant methyl sulphuric acid. The aqueous solution of the reaction mixture can now be further processed directly in accordance with Examples 1 to 3.

WHAT I CLAIM IS:—

1. An ampholytic material comprising a mixture of ampholytes which are polyamines containing at least four primary, secondary, or quaternary-tertiary amino groups as basic groups and an acidic portion comprising at least one phosphonic acid group or a mixture of sulphonic and phosphonic acid groups, the ratio of basic to acidic groups being different in different ampholytes.

2. An ampholytic material as claimed in claim 1 also containing carboxylic acid groups.

3. An ampholytic material as claimed in claim 1 substantially as hereinbefore described with reference to the Examples.

4. A process for the preparation of an ampholytic material as claimed in claim 1 which comprises reacting an aqueous polyamine solution with an aqueous solution of a phosphonic acid or a phosphonate salt and, if desired, a sulphonic acid or salt thereof.

5. A process as claimed in claim 4, in which the polyamine solution containing the phosphonic acid/phosphonate and, optionally, the sulphonic acid/sulphonate is reacted with a carboxylic acid.

6. A process as claimed in claim 5 in which the carboxylic acid is acrylic acid.

7. A process as claimed in any one of claims 4—6 in which the polyamine used as the base material is first alkylated.

8. A process as claimed in claim 7 in which the polyamine is reacted in aqueous solution with a neutral alkylating agent such as dimethyl sulphate.

9. A process as claimed in claim 7 in which the polyamine is reacted in alcoholic solution with an alkyl halide and the reaction products are recovered from the resultant acid reaction by-products by treatment with a cation exchange resin.

10. A process as claimed in any one of claims 4—9 in which the amines are aliphatic amines.

11. A process as claimed in any one of claims 4—10 in which the reaction is carried out in the presence of a catalyst.

12. A process as claimed in any one of claims 4—11 in which the reaction is carried out in the presence of an anti-oxidant.

13. A process as claimed in any one of claims 4—12 substantially as hereinbefore described with reference to the Examples.

14. Ampholytic materials according to claim 1 when obtained by a process as claimed in any one of claims 4—13.

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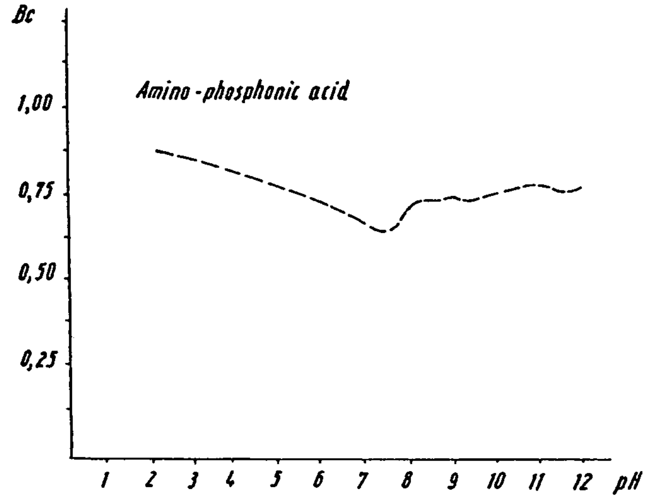

Fig. 1 Relationship of buffer capacity to pH

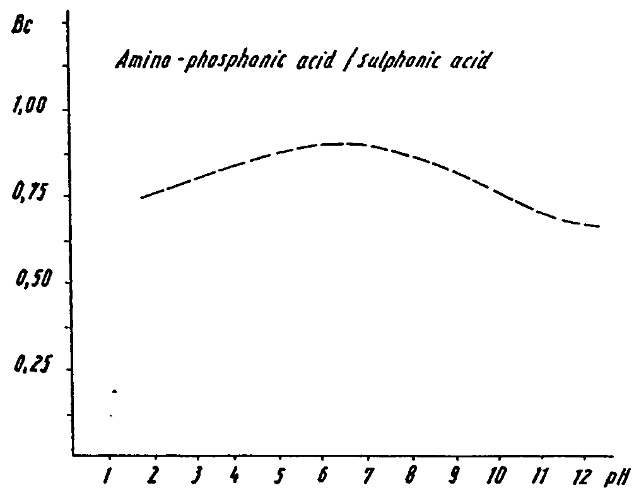

Fig. 2 pH-Relationship of buffer capacity

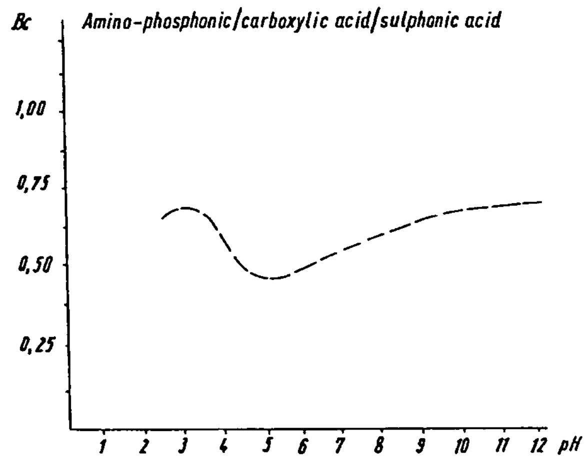

Fig.3 pH-Relationship of buffer capacity